



Faculty of Resource Science and Technology

THE USE OF SAGO WASTE FOR OIL SPILL REMOVAL

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The work described in this Final Year Project, entitled

“The Use of Sago Waste for Oil Spill Removal”

is to best of the author's knowledge that of the author except where due reference is made

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ABSTRACT

In developing countries, many industries are operating at small or medium scale, or even as a family business within the residential premises. These smaller units can generate a pollution load which in many cases, is discharged directly into the environment without any treatment. Sorbent materials such as organic synthetic products, organic vegetable products and mineral products are used to remove oil. Therefore, the aims of this study were to investigate the ability of sago waste to remove used engine oil and diesel oil in 3 types of adsorption systems, namely dry, wet static and wet dynamic systems and to determine the optimum size of sago waste for oil adsorption. Results showed that, the sorption capacity for both oils was increased with the increasing of sorption time namely, 5, 10, 15, 20, 25, 30 and 35 minutes. The sorption capacity of sago waste in three different systems followed the general trend: wet dynamic > dry > wet static. The optimum size of sago waste for oil sorption was 300 μ m. Overall, the hydrophilic nature of sago waste has influence the sorption capacity of oil.

Key words: Sago waste, oil, sorption, sorbent

ABSTRAK

Di negara membangun, terdapat banyak industri yang beroperasi pada skala kecil, sederhana ataupun hanya perniagaan keluarga di kawasan penempatan. Unit kecil tersebut boleh menghasilkan bahan pencemaran dan dalam kebanyakan kes, ia dibuang terus ke alam sekitar tanpa perawatan. Bahan penyerap seperti produk sintetik organik, produk sayuran organik dan produk mineral digunakan untuk menyerap minyak. Oleh sebab itu, objektif kajian ini adalah untuk mengkaji kebolehan hampas sago menyerap minyak diesel dan minyak pelincir terpakai dalam tiga jenis sistem iaitu sistem kering (tanpa air), sistem basah statik dan dinamik dan juga untuk menentukan saiz optimum hampas sago bagi penyerapan minyak. Hasil kajian ini menunjukkan kemampuan hampas sago untuk menyerap minyak semakin meningkat dengan pertambahan masa penyerapan iaitu 5, 10, 15, 20, 25, 30 dan 35 minit. Kemampuan hampas sago menyerap minyak dalam tiga sistem tersebut mengikut hala berikut: sistem basah dinamik > sistem kering > sistem basah statik. Saiz optimum hampas sago untuk penyerapan minyak adalah 300 μ m. Secara keseluruhan, sifat hidrofilik hampas sago mempengaruhi kadar penyerapan minyak.

Kata kunci: Hampas sago, minyak, serapan, penyerap

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List of Abbreviations

Appl	- Applied
Chem	- Chemistry
Wat	- Water
Res	- Research
Sci	- Science
Tech	- Technology
J	- Journal
km	- Kilometer
COD	- Chemical oxygen demand
BOD	- Biological oxygen demand
TOC	- Total organic carbon
m	- Meter
μm	- micrometer
ml	- millimeter
h	- hour
min	- minutes

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CHAPTER 1

INTRODUCTION

In developing countries, many industries are operated at small or medium scale, or even as a family business within the residential premises owner. These smaller units can generate a pollution load which in many cases, is discharge directly into the environment without any facilities for waste water treatment (Quek *et al.*, 1998). Used oils such as lubricating oil, metal cutting oil, machine oil, mineral oil are composed mainly of hydrocarbons and considered as toxic oily wastes.

They are called toxic because they contain heavy metals such as lead, cadmium, zinc, arsenic, as well as aromatic and naphthenic compounds (Gourgouillion *et al.*, 2000). Oily waste released directly or indirectly from food industries into water environment contain lipid which form a layer on the surface of effluents that limits the exchange of oxygen between water and air. In such cases, the microflora employed for the organic matter degradation, in an aerobic pond system, is less efficient (Haussard *et al.*, 2003).

The major problem occurs when water is contaminated by oil products because these organic compounds can cause hazards for human health. Some of the examples of these organic compounds are benzene, toluene, ethylbenzene and mixture of xylenes (BTEX) which are also known as monochromatic hydrocarbon compounds and are very toxic and often classified as carcinogens for humans (Pohl *et al.*, 2003). Although oil spills from tankers and other shipping activities by accidently, only account for 8% of total oil pollution, the impacts usually unpredictable and large (Orbell *et al.*, 2007).

Natural processes such as evaporation, oxidation, and natural biodegradation can be used to remove oil (EPA, 2004). However, this method consumes more time since it can take about many years for oil to degrade completely (EPA, 2004). This concern has resulted in the need for improved techniques and methods to overcome the problem above. Another alternative has been studied to overcome the problem by using sorbent materials. The important properties of sorbents are retention over time, amount of oil sorbed per unit weight of sorbent, recovery of oil from sorbents, and reusability and biodegradability of sorbents (Schatzberg, 1971; Halligan *et al.*, 1976; Melvold *et al.*, 1988).

Oil sorbent materials that can be used are organic synthetic products, organic vegetable products and mineral products such as perlite and sorbent clay (Schatzberg, 1971). The most commonly used sorbents in the remediation of oil spills are synthetic products such as polypropylene, polyethylene, polypropylene booms and polyurethane foam which have highly oleophilic and hydrophobic properties (Schatzberg and Jackson, 1972; Herrick *et al.*, 1982; Schrader, 1991). However, these materials degrade very slowly relative to minerals and organic vegetables and the residue are nonbiodegradable material contaminates the environment (Schrader, 1991).

The limitation of the material mentioned above has led to the study of alternative methods for oil removal using biodegradable materials such as lignocellulosic fibers (Anthony, 1994). Moreover, this material is inexpensive and readily available compared to synthetic products. According to Schatzberg, (1971), some of the organic vegetables such as rice straw, corn cob and wood fiber show poor buoyancy characteristics, low hydrophobicity and low oil sorption capacity. However, unsoured, unbleached natural fibers such as kapok [*Cheiba pentandra* (L.) Gaertn.], milkweed and cotton have greater potential as sorbent in remediation of oil spills (Johnson *et al.*, 1973; Choi and Choi, 1992; Choi *et al.*, 1993).

For example, kapok fiber has been proven to be used effectively to recover oil spilled in bodies of water such as in lakes, rivers, and oceans (Hori *et al.*, 2000). This is because of the characteristic of fiber which can absorb oil immediately. Beside that, there was another experimental investigation of various vegetable fibers as sorbent materials for oil spills. Different vegetable fibers such as mixed leaves residues, mixed sawdust, sisal (*Agave sisalana*), coir (*Cocos nucifera*), spongegourd (*Luffa cylindrica*) and silk-floss (*Chorisia speciosa*) fibers can be used as a sorbents of crude oil (Annunciado *et al.*, 2005).

Sago waste or 'hampas' is an inexpensive, copious fibrous residue left behind after most of the starch has been washed out of the rasped pith of the sago palm (Singhal *et al.*, 2008). Chew and Shim, (1993) has revealed that a large number of starch granules to be trapped within the lignocellulosic matrix through microscopic examination. According to Phang, *et al.* (2000), the sago waste may be used as animal feed, compost for mushroom culture, for hydrolysis to confectioners' syrup and for particleboard manufacture. The rice-straw mushroom (*Volvariavolvacea*), considered a delicacy in the Moluccas can be cultivated on the sago waste as well (Chang, 1980; Chang & Buswell, 1996; Chang & Miles, 1989).

Sago waste also has been used as an additional carbon in anaerobic digesters for the production of biogas (Aziz *et al.*, 2004). The sago waste and wastewater after the separation of starch from the pith is usually discharged into the rivers, where each factory producing about 10-22 tons wastewater per day (Phang *et al.*, 2000). This can lead to water pollution and affect aquatic organisms. In order to prevent this from happen, sago waste can be utilized as a sorbent material and also as mention above. This is due to the fiber residues from sago waste which was largely composed of celluloses and lignins which have some potential as a biosorbent (Vickineswary *et al.*, 1994).

Therefore, the aims of this study were:

- 1) To investigate the ability of sago waste to remove used engine oil and diesel oil in 3 types of adsorption systems, namely dry, wet static and wet dynamic systems.
- 2) To determine the optimum size of sago waste for oil adsorption.

CHAPTER 2

LITERATURE REVIEW

2.1 Wastewater

The wastewater can be discharged directly or indirectly from variety sources such as food industries and others which was contaminated with organic and inorganic pollutants. Waste is an oil emulsion resulting from chemical processing and condensation of grease trap wastes and industrial waste oils (Bentham *et al.*, 1997). The disposal of waste oils and hydrocarbons from commerce and industry has traditionally involved incineration or consolidation (Gabriel, 1991; Kim and Gee, 1993; Grasso, 1993; Stoner, 1994). For example, a liquid waste called 'olive mill wastewater' (OMW) are arises from manufacturing process of olive oil. It came from the naturally present water as well as the process water and a soft tissue from the olive pulp and forms a very stable emulsion (Garcia *et al.*, 2000)

2.2 Oil in wastewater

According to Bentham *et al.* (1997), oil in wastewater consists of a complex mixture of hydrocarbons with significant fuel oil and lube oil fraction. Human activities such as petroleum extraction, transportation and consumption are leading to ongoing oil pollution both at sea and on land. It is estimated that 1,300,000 tonnes of oil enter the sea (NRC, 2003), and around 53% of which comes from human activities mention above (IPIECA, 2005). Oil spill has great impact on our ecosystem and wildlife populations.

For example, the Exxon Valdez oil spill in March, 1989, was reported to affect 1750km of Alaskan shoreline (Tumeo *et al.*, 1994) and killed more than 30,000 seabirds (Piatt *et al.*, 1990). Based on previous studies by Kawahara, (1969); Frankenfeld, (1973); Larson *et*

et al., (1977); Payne and Phillips, (1985), showed that photooxidation of oil in the aquatic environment lead to the formation of numerous oxidation products such as aromatic, aliphatic, benzoic and naphthanoic acids, alcohols, phenols and aliphatic ketones.

2.2.1 Types of oil in wastewater

Food industries and restaurants generate an estimated 450,000 m³ of oily wastes per year (Lauzanne *et al.*, 1989) and these wastes are directly or indirectly discharged in the water environment. Used oils such as lubricating oil, metal cutting oil, machine oil, mineral oil are composed mainly of hydrocarbons and considered as toxic oily wastes. They are called toxic because they contain heavy metals such as lead, cadmium, zinc, arsenic, as well as aromatic and naphthenic compounds (Gourgouillion *et al.*, 2003).

2.2.2 Environmental impacts of oils in wastewater

Oily waste released from food industries into water environment has limits the exchange of oxygen between water and air because the lipids which are lighter from water form a layer on the surface of effluents. In such cases, the microflora employed for the organic matter degradation, in an aerobic pond system, is less efficient. This limits the decrease of chemical oxygen demand (COD), biological oxygen demand (BOD) and total organic carbon (TOC) in the treated effluents (Haussard *et al.*, 2003).

The major problem occurs when water is contaminated by oil products because these organic compounds can cause hazards for human health. Some of the examples of these organic compounds are benzene, toluene, ethylbenzene and mixture of xylenes (BTEX) which are also known as monochromatic hydrocarbon compounds are very toxic and often classified as carcinogens for humans (Pohl *et al.*, 2007).

2.2.3 Available technology for removal of oil from wastewater

There are several methods can be used for the cleaning up of oil spills from shoreline, depending on the nature of the shoreline and the nature of the affected biological communities (EPA, 2004). Natural processes such as evaporation, oxidation, and natural biodegradation can be used to remove oil (EPA, 2004). However, this method consume more time since it can take about many years for oil to degrade completely (EPA, 2004).

Other approach involves physical techniques like high pressure water flushing of oil into plastic trenches and the collection of the oil by adsorbent materials. Physical removal of the uppermost contaminated layers has to be carried out and involves aggressive techniques such as raking and bulldozing followed by the flushing process if the oil has penetrated into sand (EPA, 2004).

These techniques are labour intensive, consume time and energy (Fernandez-Alvarez *et al.*, 2007) and also generate a lot of waste which is difficult to collect and dispose of (Mateo *et al.*, 2005). The technology available for treating monochromatic contaminated water is biological methods or bioremediation. This technology appears to be potentially economically, energy efficient and environmentally sound approach (Vidali, 2001; Shim *et al.*, 2002). Bioremediation is defined as the elimination, attenuation or transformation of polluting or contaminating substances by the use of biological processes (Lynch and Moffat, 2005).

Another alternative is to use Kapok [*Ceiba pentandra* (L). Gaertn.] fiber to recover oil spill in bodies of water such as lakes, rivers, and oceans (Hori *et al.*, 2000). This Kapok fiber is significantly hydrophobic and does not wet with water in the absence of an organic solvent such as ethanol and acetone. Beside that, various different of vegetable fibers such as mixed leaves residues, mixed sawdust, sisal (*Agave sisalana*), coir (*Cocos nucifera*), spongegourd (*Luffa cylindrica*) and silk-floss (*Chorisia speciosa*) fibers can act as sorbents of crude oil

(Annunciado *et al.*, 2005). These alternative will save cost of production and time to remove oil spill.

2.3 Sago

Sago palm is belonging to the Palmae family and a species of the genus *Metroxylon*. It is a socio-economically important crop in South-East Asia and its centre of diversity is believed to be New Guinea (Rauwerdink, 1986) or the Moluccas (Ehara *et al.*, 2002). The sago palm grows well in humid tropical lowlands, up to an altitude of 700 m. Temperatures above 25°C and relative air humidity of 70% are favorable. Incidental light should preferably be above 800 k/cm² per day and salinity should not exceed 10 S/m, which is equivalent to one-eighth of the salt concentration of sea water.

Nowadays, sago palm is gaining much importance as a crop par excellence and a starch crop of the 21st century, due to over the probable global food shortage in the years to come. Besides, it is an extremely sustainable plant with ability to thrive in most soil conditions (Singhal *et al.*, 2008). Tamil Nadu state is the largest producer of sago from the cassava plant which is situated at India.

Malaysia is one of the countries in the world which exports 25000 to 30000 t of sago flour annually and tend to discharge the residues from its production to rivers. These residues are known as both waste and a pollutant and are largely composed of celluloses and lignins (Vikineswary *et al.*, 1994). Sago waste is known as a light and fluffy material generated in the preparation process of sago which is made up of cellulose, hemicellulose and lignin (Namasivayam and Periasamy, 1993; Kadirvelu, 1998). The composition of sago waste is shows in table 1.

Table 1: Composition of sago waste

Component	%
Starch	65.7
Crude fiber	14.8
Crude protein	1
Fat	n.d
Ash	4.1
Moisture	59.1

(Aziz *et al.*, 2004)

2.3.1 Sago processing

The sago processing involves few steps before the hampas or waste is dispose of. First of all, the sago logs are bringing to the factory and undergo a few steps starting with debarking the logs, and then followed by pulping. After that, starch is extract from the sago itself and the residual which also known as the sago waste or hampas is disposed.

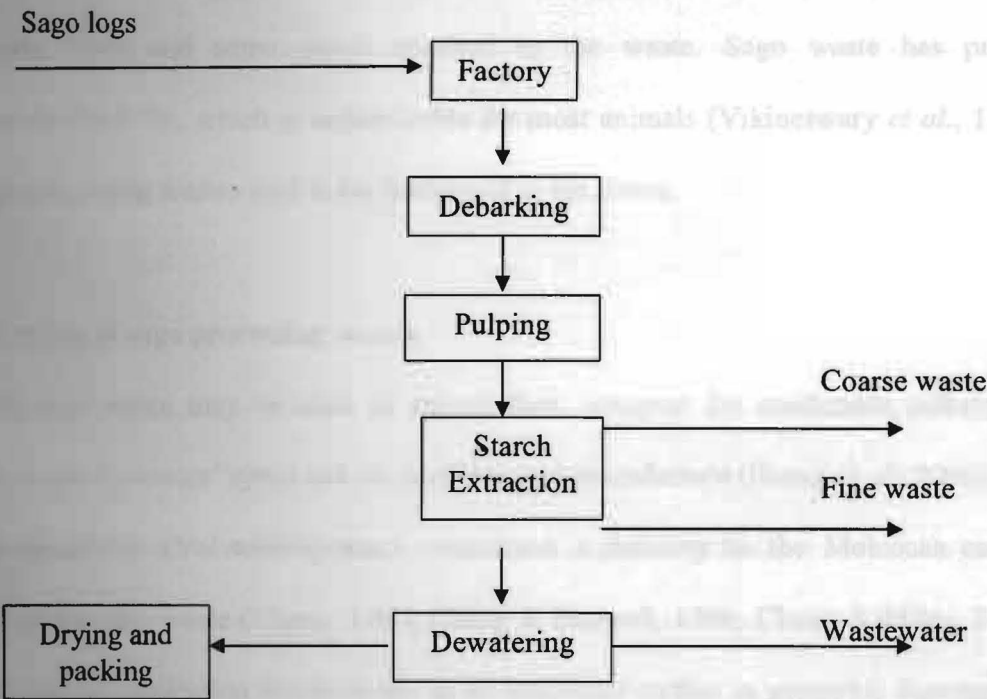


Figure 1: Schematic diagram for sago processing (Yean and Lan, 1993)

The waste can be divided into two types, namely coarse waste and fine waste. Then, the starch is dried and packed so that it can be used. During the process of dewatering, it will produce wastewater (Yean and Lan, 1993).

2.3.2 Sago processing by products/wastes

Recently, the production of sago palm starch has increased considerably. It is due to the multipurpose of starch. It can be used as a stabilizer and thickener and as a substitute for modified corn starch. Besides that, it also can be used as to produce adhesives for paper, textiles, and plywood; as a stabilizer in pharmaceuticals; or converted to other types of foods.

Nowadays, it is used as an economically viable feedstock for conversion to industrial sugars, and the market for sago is set to expand both as a domestic food and as a trade crop. Meanwhile, sago pith and subsequently sago waste has very low nutrient content and the bulk being crude fibres and some starch attached to the waste. Sago waste has protein approximately 0.6-0.7%, which is unfavourable for most animals (Vikineswary *et al.*, 1994). These sago processing wastes tend to be discharged in the rivers.

2.3.3 Utilization of sago processing wastes

The sago waste may be used as animal feed, compost for mushroom culture, for hydrolysis to confectioners' syrup and for particleboard manufacture (Phang *et al.*, 2000). The rice-straw mushroom (*Volvariavolvacea*), considered a delicacy in the Moluccas can be cultivated on the sago waste (Chang, 1980; Chang & Buswell, 1996; Chang & Miles, 1989). Another important application lies in its use as an additional carbon in anaerobic digesters for the production of biogas (Aziz *et al.*, 2002).

The utilization of sago processing wastes for activated carbon synthesis may give a solution to solid waste management in the sago industry and in other industries, which require the removal of pollutants (Kadirvelu *et al.*, 2004). Activated carbon adsorption has been widely used to remove pollutants from wastewaters. However, commercially available carbons in market are very expensive, so there is a need to find other alternative to produce low cost, disposable activated carbons (Streat *et al.*, 1995) and sago waste are used as a source of activated carbon.

The result obtained from an experiment of mercury (II) adsorption by activated carbon made from sago waste by Kadirvelu *et al.* (2004) show that carbon preparation from sago waste can be used for the removal of mercury from aqueous solution. Apart from that, it has the potential substrate for microbial conversion via solid substrate fermentation into value added products such as enzymes (Singhal *et al.*, 2008). Besides that, sago processing waste can also be used as a substrate for the production of laccase by solid substrate fermentation (SSF) with *Pleurotus sajor-caju* (Kumaran *et al.*, 1997). The fiber residues from sago waste was largely composed of celluloses and lignins which have some potential as a biosorbent (Vickineswary *et al.*, 1994).

2.3.4 Sago waste for oil removal

Sago waste is an inexpensive, copious fibrous residue left behind after most of the starch has been washed out of the rasped pith of the sago palm (Singhal *et al.*, 2008). The fiber residues from sago waste was largely composed of celluloses and lignins which have some potential as a biosorbent (Vickineswary *et al.*, 1994).

According to some research, there were various vegetables fibres were used as sorbent materials for oil spills (Annunciado *et al.*, 2005). For example mixed leaves residues, mixed sawdust, sisal (*Agave sisalana*), coir (*Cocos nucifera*), spongegourd (*Luffa cylindrica*) and silk-floss (*Chorisia speciosa*) fibers.

The experiment conducted has proven that the fibre contain in the vegetables fibre can adsorb oil and the sorption capacity of the fibers followed the general trend: silk-floss > sisal and sawdust > coir fiber > sponge gourd > leaves residues and the sorption capacity may be further increased by reducing granulometry (Annunciado *et al.*, 2005). Beside that, there was also a study done by Hori *et al.* (2000) on kapok fiber to determine whether kapok fiber could be used effectively to recover oil spilled in bodies of water such as in lakes, rivers, and oceans.

Based on the research, kapok fiber is significantly hydrophobic and does not wet with water in the absence of organic solvent such as acetone and ethanol. However, the significantly high hydrophobicity and oil absorptivity are not due to the components of the kapok fiber because the treated kapok fiber give same result as original kapok fiber. This study has shown that kapok fiber can be used effectively to recover oil spill (Hori *et al.*, 2000).

Moreover, there was a study done by Lee *et al.* (1999) on oil sorption by lignocellulosic fibers such as cotton fiber, kenaf bast fiber, kenaf core fiber and moss fiber. These sorbent materials were compared after refining, extraction and reduction in particle sizes. Based on the result, cotton shows the highest capacity of oil sorption among the fibers examined. This sorption is due to the large amount of wax on the fiber surface, the hollowed surface and the larger, noncollapsing lumen of the fiber.

Furthermore, there was a study done by Suni *et al.* (2004) on use of a by-product of peat excavation, cotton grass fibre, as a sorbent for oil spills. The studies has shown that, cotton grass is an excellence sorbent for various types of oil. The cotton grass sorbent adsorbed approximately three times as fast and at least as much of each oil as the synthetic one. It is also very suitable sorbent product because it adsorb very little or no water. Besides that, it will float on water and even after one week in oily water, it did not sink due to its density which is also low.

CHAPTER 3

MATERIALS AND METHOD

3.1 Material

The sago waste was collected from Nitsei Sago Sdn. Bhd in Mukah, Sarawak. Before the sago waste can be used in the experiment, the sago waste was grinded in a food processor, drying in an oven at 105⁰C for 24 h, and then screened through 14 mesh sieves. This was done to remove any large particles and to obtained adsorbents with a known particle size range. The sieved material was prepared in two different ranges of sizes which are 500 µm and 300 µm. After that, the sieved materials were stored in an airtight plastic container for further experiments (Quek et al., 1998).

3.2 Characterization of sample

3.2.1 Apparent density

Approximately 5.0 g of 500 µm sago waste was put into a syringe and compressed. Then, the volume of sample which has been compressed was recorded. This was done for triplicate sample. After that, the above method was repeated for 300 µm of particle size. A clean 50 ml measuring cylinder was weighted on analytical balance and tare. After that, used engine oil was poured into the measuring cylinder until the reading has shown approximately 10 ml. The weight of the oil was recorded. This was done for triplicate sample. The apparent density for both sago waste and used engine oil were calculated by using the formula below:

$$\text{Apparent Density} = \text{Mass (kg)} / \text{Volume (m}^3\text{)}$$